

CHARGE CARRIER DYNAMICS OF ANATASE TiO₂ PROBED BY EXTREME ULTRAVIOLET REFLECTION-ABSORPTION SPECTROSCOPY

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Materials with improved catalytic efficiency can be designed based on a more thorough understanding of the excited state dynamics that mediate energy transfer and drive charge separation. High harmonic generation can produce ultrafast pulses in the extreme ultraviolet (XUV) region, enabling the use of XUV reflection-absorption (XUV-RA) spectroscopy to analyze signatures of photoexcited electrons and holes separately. From XUV-RA experiments on anatase TiO₂, it is shown that, for the first 800 fs after photoexcitation there is an apparent quantum beating at 417 cm⁻¹. This frequency is consistent with coupling between a free carrier state and a large polaron state, which has been previously observed in TiO₂. Following the initial dynamic equilibrium between these two states, the electron localizes to a more energetically stable Ti³⁺ defect state 1 eV below the conduction band within 1.22 ps. We hypothesize that the strong electron-phonon coupling leading to the observed beating may be the result of Ti³⁺ defect states which we show are prevalent in this material. To investigate this hypothesis, we are now performing measurements on stoichiometric TiO₂ with Ti³⁺ defects removed. These ongoing experiments on defect-free TiO₂ will provide a more complete understanding of the role the Ti³⁺ defects play in the charge carrier kinetics of this catalytically relevant material.